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Single-Crystal Studies of β-Ag_2HgI_4*

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The structure and transformation behavior of β-Ag_2HgI_4 have been investigated by X-ray diffraction methods using single crystals. It has been verified that a single crystal of the β-form, stable at room temperature, transforms to a single crystal of the α-phase, stable above 50°C. The reverse transformation, $\alpha \rightarrow \beta$, on the other hand, is found to result in a multidomain arrangement of the β-phase and not to yield a new cubic modification. The β-structure is tetragonal: $a = 6.322$ (2) Å, $c = 12.605$ (15) Å, with space group $I\bar{4}$ and $Z = 2$. The chalcopyrite type of cation ordering, proposed by Hahn *et al.* (*7*), is confirmed. The iodine arrangement is considerably distorted from ideal cubic close packing with preservation of normal cation–iodine distances. No significant amount of disorder or occupancy of vacant sites has been found.

Introduction

Despite the many studies of the structure and properties of Ag_2HgI_4 since the pioneering work of Ketelaar (*1–5*), there remains much confusion and uncertainty regarding both the structure and the behavior, physically and chemically, of this substance. With only one exception (*6*), the investigations have been made with polycrystalline specimens. Accordingly, we have undertaken to obtain more definitive results for the structural situation as well as for the conductivity and transformation behavior of Ag_2HgI_4 by using single crystals. The present report concerns itself with the crystal structure of the room-temperature or β-form and some aspects of the transformation to and from the α-form, stable above 50°C, based on the results of X-ray diffraction studies.

It is generally accepted that the unit cell of the β-form is tetragonal, but not pseudocubic (with $a = c = 6.34$ Å), as originally proposed by Ketelaar (*1*). Several investigators, most notably Hahn *et al.* (*7*), Hoshino (*8*), and Olsen and Harris (*6*), have found that the c dimension is twice that of the pseudocubic cell. Furthermore, Hahn *et al.* (*7*) deduced a plausible structure, although not refined, that accounted satisfactorily for the measured powder intensities. This is shown in Fig. 1. Olsen and Harris (*6*), the only investigators who have used single crystals, agreed as to the unit cell and space group reported by Hahn *et al.* (*7*) but reached different conclusions as to details of structure, although modern methods of structure refinement were not used. While there is a concensus on the tetragonality of the unit cell, Frevel and North

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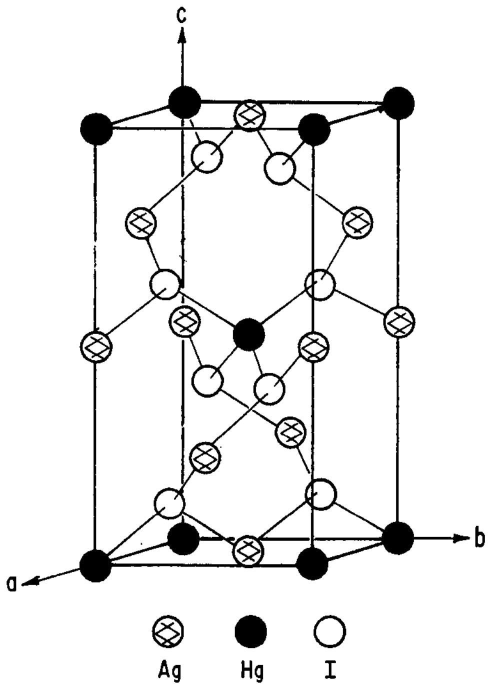

FIG. 1. The structure of β-Ag_2HgI_4.

(9) have reported a cubic cell with $a = 12.62$ Å.

Regarding the possibility of more than one room-temperature phase of Ag_2HgI_4, it has been claimed (6) that the phase produced from solution below the transition temperature, which is tetragonal with $a = 6.32$ Å, $c = 12.64$ Å, is never again obtained during cycles of heating and cooling through the transition temperature; instead a new phase, which is cubic with $a = 12.64$ Å, was said to be formed. The latter was considered to be the more stable phase and was called β, whereas the term β' was given the more familiar tetragonal form. Our investigation establishes the incorrectness of the claim for the cubic phase. There is then only the one tetragonal room-temperature phase for which we retain the designation β, as has been done by others.

Preparation and Stability of Crystals

Synthesis and crystal growth. Silver iodide, AgI, was obtained as the purified salt from Alfa Inorganics. Mercuric iodide, HgI_2, and potassium iodide, KI, were reagent grade from Fisher Scientific. All materials were used without additional purification.

Single crystals used in this study were grown by a technique based on a report by Olsen and Harris (6), although successful crystal growth required some modification of their procedure: A concentrated solution (3.0 *M*) of K_2HgI_4 was prepared and then nearly saturated first with respect to HgI_2 and then with respect to AgI. The solution was then transferred to a test tube 24 mm in diameter and 190 mm in length to a level about one-third full. Distilled water was then carefully poured into the tube and floated on top of the more-dense reactant solution. Care was taken to avoid any mixing of the two layers. The tube was stored in the dark for 4 weeks at room temperature. At the end of this time, numerous yellow crystals had formed in the bottom layer. These were removed and washed with 2.0 *M* K_2HgI_4, then with 0.1 *M* K_2HgI_4 (to remove excess HgI_2), and finally with distilled water. Most of the crystals were well-formed long, thin, yellow needles of approximate dimensions 1 × 0.05 × 0.02 mm. However, some very thin yellow rectangular plates were also noted.

The key to successful Ag_2HgI_4 crystal growth seems to be in using a very large excess of HgI_2. It is for this reason that the K_2HgI_4 solution is saturated first with respect to HgI_2. A consequence of this is that many red HgI_2 crystals are formed along with the yellow Ag_2HgI_4 crystals. In preparations where too much AgI had been added (i.e., insufficient excess of HgI_2), no Ag_2HgI_4 crystals were formed.

The morphology of the needles was as reported by Olsen and Harris (6), with $\langle 110 \rangle$ always the needle axis, and with prominence of $\{112\}$ and $\{001\}$ faces. Twinning was observed for many of the crystals, most notably with the $\langle 112 \rangle$ direction as the twin axis.

Stability of crystals. A great variability in the stability of different crystals was experienced. Not only obviously poor specimens exhibiting considerable strain, but also some crystals with well-developed faces and yielding good Laue patterns were found to deteriorate in a period of weeks or months. It was ascertained that one problem, especially upon heating the crystals in air, was the tendency to lose HgI_2; accordingly, for the experiments above 50°C, the crystals were enclosed in thin-walled closed capillaries. There seemed to be other causes and other mechanisms, however, for the deterioration of crystals. Generally, loss of HgI_2 results in a color change from deep yellow to very light yellow, but a variety of other color changes also were shown by some specimens; these ranged from deep brown to black. The possible effect of light was considered and a general precaution was to minimize exposure to light but no definite effect of light could be established. The whole matter of instability of the crystals appears to be quite complex and would require further extensive research. We can only suggest that the crystals may be very sensitive to defects associated perhaps with small deviations from stoichiometry. Empirically, it appeared that the most stable crystals resulted from the use of excess HgI_2 in their preparation.

It has been possible, nonetheless, to obtain crystals that remain stable for long periods of time (months). The particular crystal used for the structure determination and some of those used for the transformation studies were such examples. It is a necessary, but not sufficient, condition for stability that the crystals appear to be of the highest quality both optically and with respect to their X-ray diffraction patterns.

Transformation Studies

One of the intriguing results reported by Olsen and Harris (*6*) was that the $\beta \rightarrow \alpha$ transformation yields a single crystal of the α-form when a crystal of the β-form is heated above the transformation temperature. If true, there is then the rare opportunity of obtaining single-crystal structural data for a three-dimensional ionic conductor (of the classic type with a simple anion arrangement) in its conducting state. We have verified this finding mainly with the X-ray precession technique and have even made a detailed study of the α-structure which we shall report subsequently. For the present, we only wish to note that the quality of the formed α-crystal is essentially the same as of the starting β-crystal. The mosaic spread, for example, was found to be typically 0.5 degree for both forms. It should not be surprising that the $\beta \rightarrow \alpha$ transformation can give a good single crystal since there is essentially no volume change associated with the transformation during which the same iodine framework is preserved and the main structural change is a disordering of cations among the tetrahedral sites.

On the other hand, we find that contrary to the report by Olsen and Harris (*6*), no new structure is formed by cooling a crystal of the α-phase to room temperature. The transformation is an $\alpha \rightarrow \beta$ transition but the special multidomain character of the resultant β-phase can give the erroneous impression

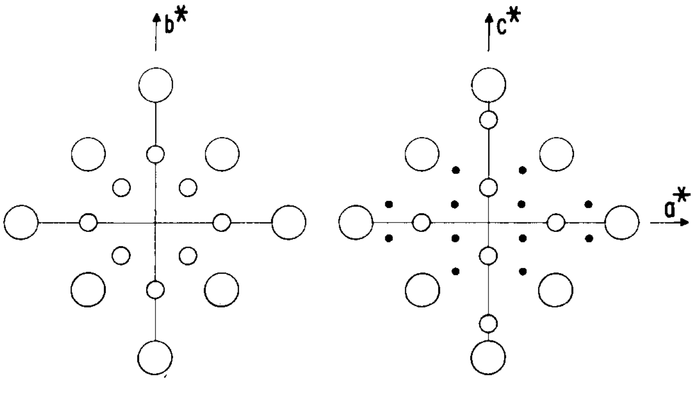

FIG. 2. The *hk*0 and *h*0*l* reciprocal lattice nets of β-Ag_2HgI_4 before heating.

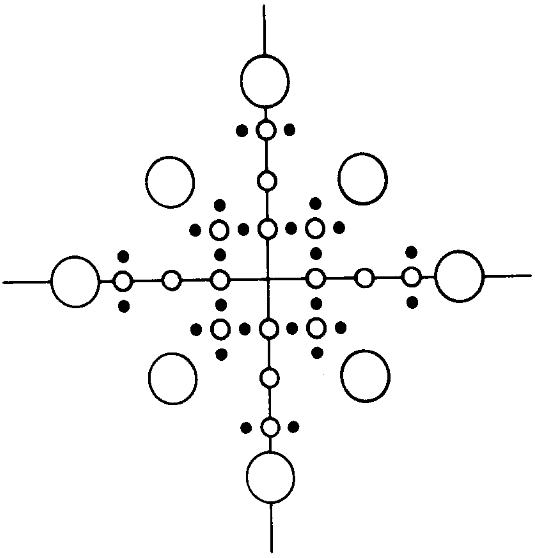

FIG. 3. Schematic reciprocal lattice net for β-Ag_2HgI_4 after heating.

under certain circumstances of a cubic structure with $a = 12.64$ Å. The details of the transformation behavior are illustrated in Figs. 2 and 3, which are idealized schematic reciprocal lattice diagrams corresponding to precession photographs taken with Mo*Kα* radiation. Figure 2 shows the *hk*0 and *h*0*l* reciprocal lattice nets for the β-phase before heating, and Figure 3 shows the one net obtained for both orientations after heating beyond the transformation point. Three classes of reflections are depicted, the size of the circle being proportional to the intensity of the reflection. Figure 2 illustrates how the tetragonality, i.e., the distinction between b^* and c^*, is due to weak reflections only, the strongest ones occurring in the same relative positions (note that $2c^*$ is essentially a^* dimensionally). In the transformation to the α-phase, which is truly cubic, each of three axes, a^*, b^*, c^*, becomes an equivalent a^* of the α-structure. In the reverse transition, $\alpha \rightarrow \beta$, we find that any of three cubic axes of α can become the c^* axis of β in different regions of the crystal. If all three axes are equally operative, the resultant diffraction pattern is that shown in Fig. 3, which is produced by superposition of the three nets of the β phase, where c^* is successively chosen along three orthogonal directions. Although superficially cubic in appearance, it is in fact the superposition pattern for a multidomain specimen of ordinary β-Ag_2HgI_4. It is this pattern which has been observed for the alleged new cubic phase with $a = 12.64$ Å.

Actually, in our experience, the occurrence of the three domains in equivalent amounts was rather infrequent. It was more typical to find different proportions for the domains, and in more than one case only one domain predominated. It is these latter observations that make clear that the transition is indeed $\alpha \rightarrow \beta$ and that there is only one room-temperature structure, namely, the tetragonal β-structure.

Structure Determination

The crystal used for the detailed structure investigation was a needle (needle axis along [110]) 0.0185 cm long and bounded by {112} and {001} faces with the dimensions given in Fig. 4. This crystal was not enclosed in a capillary but no change of intensities or other physical changes were observed during the collection of X-ray intensity data at 23 ± 2°C.

The lattice parameters were determined to be $a = 6.322(2)$ Å, $c = 12.605(15)$ Å. Note that $c/a = 1.994$ and not exactly 2.000 as given in the literature. These values are

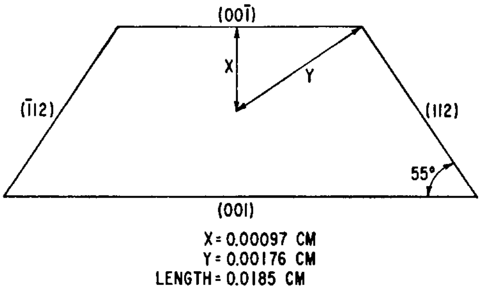

FIG. 4. Crystal dimensions.

TABLE I

ATOMIC PARAMETERS—β-Ag_2HgI_4, SPACE GROUP $I\bar{4}$–S_4^2

Atom	X	Y	Z
I (8g)	0.2652(4)	0.2284(4)	0.1332(1)
Hg (2a)	0	0	0
Ag_1 (2b)	0	0	1/2
Ag_2 (2c)	0	1/2	1/4

derived from a powder pattern taken with a focusing camera and are essentially the same as those obtained from alignment of the crystal on the diffractometer for determining angular settings. The space group is $I\bar{4}$ and $Z = 2$.

One-half the sphere of reflection with a radius of $(\sin\theta)/\lambda = 0.65$ was covered with a GE 490 automated diffractometer using Mo$K\alpha$ (0.7107 Å) radiation, monochromatized by reflection from the (002) plane of a graphite crystal. Absorption corrections ($\mu = 310.5$ cm^{-1}) and Lorentz polarization factors (appropriate for a monochromatized beam) were applied and the intensities of reflections of a given form averaged. The weighting factors (w) were determined from the counting statistics and the deviations in the measured intensities for reflections of the same form: $w = \sigma^2$, where $\sigma^2 = \sigma_c^2 + \sigma_v^2$; σ_c^2 is the counting statistics variance;

$$\sigma_v^2 = \sum_{i=1}^{m} d_i^2/m - 1,$$

m is the number of equivalent observations, and d_i is the deviation of the ith measurement from the mean value. Reflections for which the intensity was less than twice the standard deviation were rejected. The number of observed independent reflections was 269.

The programs for reduction of data, for least-squares refinement of parameters, and for Fourier series are our standard programs based on those developed at Oak Ridge and Brookhaven and are described in detail elsewhere (*10*).

Having established from the study of precession photographs that the space group and the approximate structure are those given by Hahn *et al.* (*7*), the refinement procedure was straightforward. Three cycles of least-squares refinement for the three positional parameters of iodine and the twelve anisotropic temperature factors converged with a value of

$$R = \frac{\sum||F_{\text{obs}}|-|F_{\text{calc}}||}{\sum|F_{\text{obs}}|}$$

of 0.049. The weighted R value was 0.035. The scattering factors for Ag^+, Hg^{2+}, and I^- were those of Cromer and Waber (*11*) corrected for

TABLE II

THERMAL PARAMETERS—β-Ag_2HgI_4[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.0176(3)	0.0175(3)	0.0040(1)	−0.0012(3)	−0.0000(2)	−0.0065(25)
Hg	0.0238(3)	0.0238(3)	0.0048(2)	0	0	0
Ag_1	0.0263(7)	0.0263(7)	0.0079(4)	0	0	0
Ag_2	0.0315(6)	0.0315(6)	0.0096(5)	0	0	0

[a] Anisotropic temperature factors are expressed as: $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

TABLE III

Observed and Calculated Structure Factors (×1/2) for β-Ag_2HgI_4. $F_{000} = 772$

H	K	F_{OBS}	F_{CALC}
		L=0	
0	2	29	29
0	4	168	174
0	6	9	9
0	8	33	33
1	1	66	66
1	3	52	54
1	5	27	27
1	7	15	14
2	2	220	244
2	4	14	16
2	6	70	73
3	1	58	58
3	3	22	25
3	5	34	34
4	2	15	16
4	4	93	97
4	6	8	6
5	1	17	19
5	3	40	38
6	2	73	73
7	1	22	22
		L=1	
0	1	42	36
0	3	63	58
0	5	27	30
0	7	27	26
1	2	42	46
1	4	52	54
1	6	16	18
1	8	21	21
2	1	69	74
2	5	46	42
2	7	17	20
3	2	41	41
3	4	27	30
3	6	29	29
4	1	12	13
4	3	49	51
4	5	15	18
4	7	19	19
5	2	36	33
5	4	26	27
5	6	12	13
6	1	36	38
6	3	10	9
6	5	22	21
7	2	18	21
7	4	14	13
		L=2	
0	0	57	52
0	2	76	77
0	4	30	30
0	6	26	26
1	1	210	219
1	3	149	154
1	5	81	80
1	7	34	37
2	2	41	41
2	4	42	42
2	6	16	16
3	1	149	148
3	3	112	109
3	5	61	63
4	2	44	45
4	4	24	25
4	6	19	18
5	1	82	85
5	3	62	59
5	5	38	37
6	0	26	26
6	2	18	17
6	4	23	22
7	1	36	34
7	3	29	30
		L = 3	
0	1	57	59
0	3	29	29
0	5	36	39
0	7	15	15
1	2	59	57
1	4	26	24
1	6	41	40
1	8	12	14
2	3	55	57
2	5	15	13
2	7	23	22
3	2	41	42
3	4	43	44
3	6	19	18
4	1	57	54
4	5	29	31
4	7	11	8
5	2	31	29
5	4	21	22
5	6	20	21
6	1	17	17
6	3	31	29
7	2	19	19
7	4	15	14
8	1	26	22
		L = 4	
0	0	34	32
0	2	234	245
0	4	17	17
0	6	73	74
1	1	71	71
1	3	46	44
1	5	29	31
1	7	13	13
2	2	23	21
2	4	127	129
3	1	43	45
3	3	49	49
3	5	10	12
3	7	18	17
4	2	130	129
4	4	11	11
4	6	41	44
5	1	36	36
5	5	28	26
6	4	45	45
7	3	22	21
		L = 5	
0	1	54	45
0	3	28	29
0	5	44	41
0	7	21	23
1	2	42	43
1	4	16	18
1	6	27	27
2	3	56	50
2	5	24	28
2	7	28	25
3	2	43	36
3	4	28	29
3	6	10	12
4	1	45	46
4	3	14	11
4	5	32	29
5	2	26	28
5	4	22	18
5	6	14	13
6	3	25	26
7	2	22	20
		L = 6	
0	0	96	96
0	2	14	12
0	4	55	53
1	1	155	156
1	3	113	110
1	5	64	65
1	7	27	27
2	2	72	71
2	4	12	12
2	6	25	24
3	1	116	116
3	3	87	84
3	5	47	49
3	7	24	22
4	2	13	11
4	4	35	33
5	1	63	59
5	3	51	53
5	5	29	28
6	2	26	27
6	4	14	10
7	1	29	31
7	3	22	20
		L = 7	
0	1	32	33
0	3	32	32
0	5	18	17
0	7	16	13
1	4	48	47
1	6	17	18
2	1	49	44
2	5	24	24
3	2	39	38
3	4	19	18
3	6	29	29
4	1	18	14
4	3	35	33
5	2	17	19
5	4	27	24
6	1	35	33
6	3	12	10
7	2	16	13
		L = 8	
0	0	181	178
0	2	22	21
0	4	102	100
1	1	57	53
1	3	46	47
1	5	25	23
1	7	14	13
2	2	135	132
2	4	13	13
2	6	45	45
3	1	47	44
3	3	26	26
3	5	28	26
4	2	11	14
4	4	60	59
5	1	20	23
5	3	31	27
6	2	47	46
7	1	17	15
		L = 9	
0	1	21	20
0	3	38	34
0	5	22	25
1	2	21	24
1	4	21	22
2	1	34	35
2	3	19	22
2	5	32	29
3	2	21	23
3	4	17	17
4	1	8	5
4	3	30	29
4	5	15	17
5	2	28	23
6	1	17	17
		L = 10	
0	0	11	9
0	2	65	66
0	6	23	23
1	1	89	84
1	3	67	67
1	5	38	37
2	2	10	8
2	4	39	39
3	1	66	62
3	3	50	51
3	5	29	30
4	2	39	40
4	4	11	8
5	1	40	42
5	3	31	27
		L = 11	
0	1	18	20
0	3	18	17
0	5	11	9
1	2	31	31
1	4	12	12
1	6	26	25
2	3	21	22
3	2	9	10
3	4	27	27
4	1	31	30
5	2	19	17
6	1	11	11
		L = 12	
0	0	15	15
0	2	78	79
0	4	9	10
1	1	42	44
1	3	32	30
1	5	19	21
2	2	10	12
2	4	46	48
3	1	30	33
3	3	28	29
4	2	46	48
5	1	22	20
		L = 13	
0	1	17	15
0	5	20	18
2	3	22	19
3	2	16	15
4	1	14	14
		L = 14	
0	0	46	49
0	4	31	30
1	1	40	42
1	3	29	31
2	2	37	38
3	1	31	34
3	3	23	25
		L = 15	
2	1	15	16
		L = 16	
0	0	35	39

anomalous dispersion according to Cromer (*12*). The structural parameters are given in Tables I and II, assuming the ideal composition Ag_2HgI_4. Table III lists the observed and calculated structure factors.

Possible deviations from stoichiometry were explored by allowing the occupancy factors to vary in the least-squares refinement process. These numbers differed slightly (1–2%) from the ideal values but not significantly with regard to the standard deviations. Thus, the following ratios were obtained:

$$\mathrm{Ag/I} = 0.495(8);\ \mathrm{Hg/I} = 0.244(7);\ \text{and}\ \mathrm{Ag/Hg} = 2.033(7).$$

The respective values for exact stoichiometry are 0.5, 0.25, and 2.00. The R values were identical to those for the ideal composition. It is not possible then to decide about deviations from stoichiometry to the extent of a few percent, but the results rule out such gross deviations as 10% or more.

Various electron density sections showed no significant occupancy by cations of either octahedral sites or those tetrahedral sites that are excluded by the ordering scheme of the β-structure. Two sections normal to [110], one at $x + y = 0$ and the other at $x + y = 1/2$, are shown in Figs. 5 and 6. The former contains I, Hg, and Ag_1, and the latter I and Ag_2. For purposes of clarity, the zero contour is omitted and the lowest contour shown is one-tenth that of the maximum for a silver atom. Difference Fourier synthesis did not indicate any significant modifications in the structure as presented. The largest region of positive density was close to an octahedral interstice but the amount of silver occupancy would be less than 1%.

Discussion of the Structure

There are two descriptions (*6*, *7*) of the β-structure which are at variance with respect to the details of iodine parameters, degree of ordering, and possible occupancy of octahedral sites. Our findings are in accord with those of Hahn et al. (*7*) in that there is considerable distortion of the iodine arrangement from ideal cubic close-packing and that there

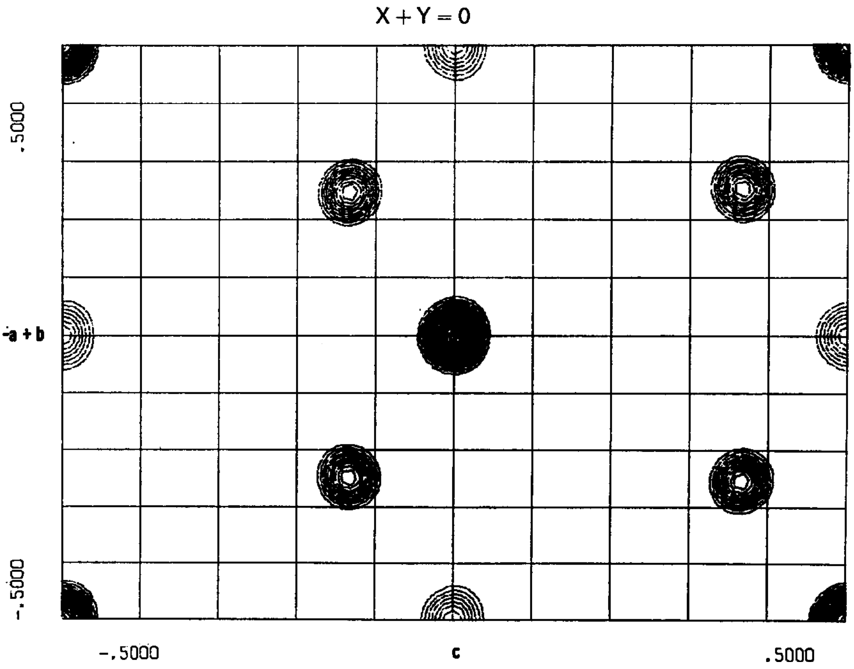

FIG. 5. Fourier section for β-Ag_2HgI_4, normal to [110] at $x + y = 0$.

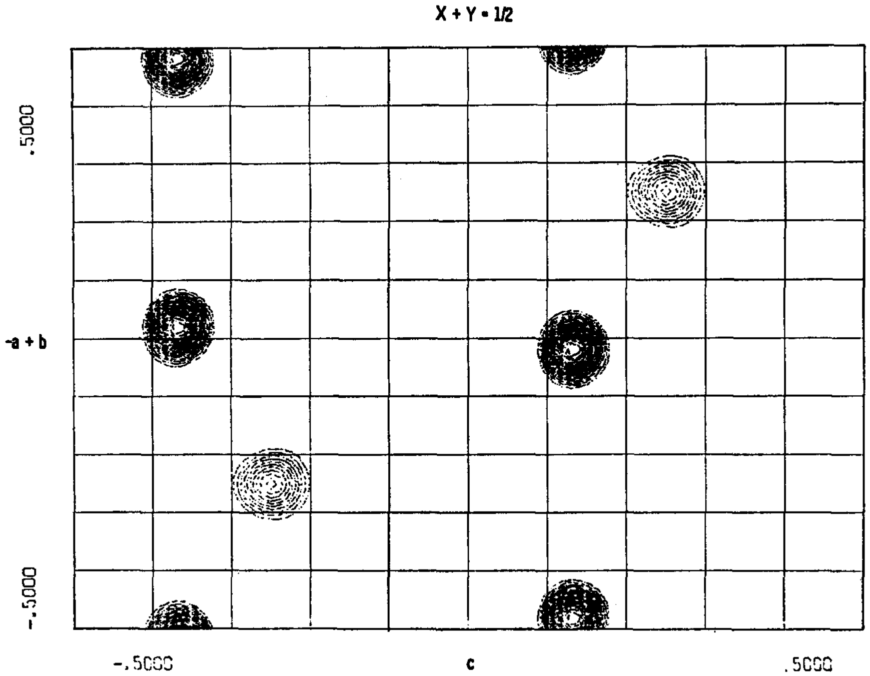

FIG. 6. Fourier section for β-Ag_2HgI_4, normal to [110] at $x + y = 1/2$.

is essentially complete ordering of the cations. The ordering scheme is that of chalcopyrite but with the omission of two sites. Olsen and Harris (*6*), on the other hand, claimed that the iodine positions were those for strict close-packing but with some vacancies and that there was significant disorder of silver atoms. It is quite conceivable that some disorder and nonstoichiometry can exist in different crystals, especially in light of our experience that many crystals as grown are far from perfect and that these, as well as seemingly good crystals, can change in composition and perfection with time. Our efforts were directed toward achieving structural data for as perfect a crystal as could be obtained and our results indicate that the particular crystal studied was not grossly disordered or far from ideal composition and, hence, represents closely the ideal structure of β-Ag_2HgI_4. That structure is well-ordered with an iodine arrangement that is quite appreciably distorted from ideal cubic close-packing.

TABLE IV

INTERATOMIC DISTANCES (Å) FOR β-Ag_2HgI_4

Hg–I	4 of 2.778(6)
Ag_1–I	4 of 2.823(6)
Ag_2–I	4 of 2.815(6)
I–I	1 of 4.425(12)
	1 of 4.539(12)
	1 of 4.142(12)
	1 of 4.800(12)
	2 of 4.590(12)
	2 of 4.645(12)
	2 of 4.153(12)
	2 of 4.493(12)

The positional parameters for iodine from our refined structure result in Hg–I and Ag–I interatomic distances (Table IV) that are in excellent agreement with those for other related compounds. In γ-AgI (*13*), the Ag–I distance is 2.812 Å, and in HgI_2 (*14*), the separation Hg–I is 2.78 Å, essentially the same distances in both cases that we have found.

The thermal parameters are somewhat large, especially for the cations, but may be realistic considering that Ag_2HgI_4 is barely stable and that cation mobility is generally high in related silver salts. It seems plausible that Ag_2 would exhibit the largest thermal motion since it occupies that site of the chalcopyrite type of arrangement whose surroundings contain the largest proportion of vacancies. This can be appreciated by considering only the cation arrangement. Whereas the shell of the twelve first-neighbor sites is similar in each case (eight cations and four vacancies around Hg, Ag_1, and Ag_2), the second-neighbor shell of six sites contains two vacancies in the case of Ag_2 and none for Hg and Ag_1.

It is anticipated that this detailed characterization of the β-form, when compared with a refined structural analysis of the α-form, will be useful in understanding the ionic conduction in Ag_2HgI_4. Work is currently in progress toward this goal.

Acknowledgment

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